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Possibilities and limitations of multioxides crystals growth

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ABSTRACT

The main methods of crystal growth from the melt the Czochralski and floating zone will be discussed and compared. Advantages, disadvantages and limitations of both methods as well as ways of solving some of the problems existing during growth of different types of multioxides crystals will be discussed.

The chemical composition of crystals grown by the Czochralski method very often differs from the stoichiometric composition. Such deviations were found and well documented in a few groups of materials for example in garnets. Since the deviation is not known for most of the crystals, a simple way to determine the optimum starting composition of the melt will be presented. In order to determine the composition of the melt one should take into account evaporation of a volatile component that dissociates at high temperatures during crystal growth.

Some problems related to the dopant distribution along the crystal growth direction in correlation with segregation coefficient for both methods will be discussed. To grow solid solution single crystals by the Czochralski method with a desired concentration of the admixture one has to know segregation coefficients of the components. A few examples of the dopant solubility limit in different crystal matrices will be presented.

1. INTRODUCTION

We will present and compare the Czochralski and floating zone methods that we use to grow single crystals. We intend to discuss advantages and disadvantages of both methods and ways of solving some of the arising problems. In particular we will show the problems involved with doping of the crystals, segregation of the dopants and methods of determining the dopant concentration in the crystals.

2. ADVANTAGES AND LIMITATIONS OF THE FLOATING ZONE METHOD

The compounds melting incongruently with a peritectic reaction, at the melting point decompose into the substance remaining in solid phase and the liquid with the composition corresponding to the peritectic point. Compounds of the composition only slightly differing from the peritectic point may still be crystallized by the Czochralski method if the process is started with the melt of the peritectic point composition. Then the composition of the melt will change from the peritectic to eutectic one during the crystal growth.

To the other important class of compounds belong systems in which the starting substances form solid solutions. It is obvious that the crystal and the melt composition change during the crystal growth by the Czochralski method.

The floating zone method allows one to crystallize not only congruently melting materials but also a lot of compounds exhibiting peritectic point reaction. In this method only a small part of the ceramic material is melted. The equilibrium state is reached very soon after beginning the process, yet the crystal and the melted rod have the same composition while the molten drop composition corresponds to the peritectic point. Thus in contrast to the Czochralski method, it may be applied to much wider range of materials. The segregation of the dopant is less important here and influences the dopant concentration only at the beginning and at the end of the crystal.

Also during growth of solid solution crystal by this method, equilibrium is soon reached with the same composition of the crystal and the ceramic rod, while the molten zone has another composition depending on segregation coefficient between components.

Since this method does not require any crucible, it may be used to grow crystals with higher melting temperatures. Thus, the problems of reaction between the melt and crucible are avoided. In principle, the crystallization may be carried out in any atmosphere even in air or oxygen consequently decreasing dissociation of the melt. It further extends the range of materials that may be crystallized, to those melting congruently but strongly dissociating.

The main disadvantage of the floating zone method results from the large temperature gradient along the crystal, from the growth region to the part previously crystallized. In consequence, the quality of the crystals is lower than those grown by the Czochralski method.

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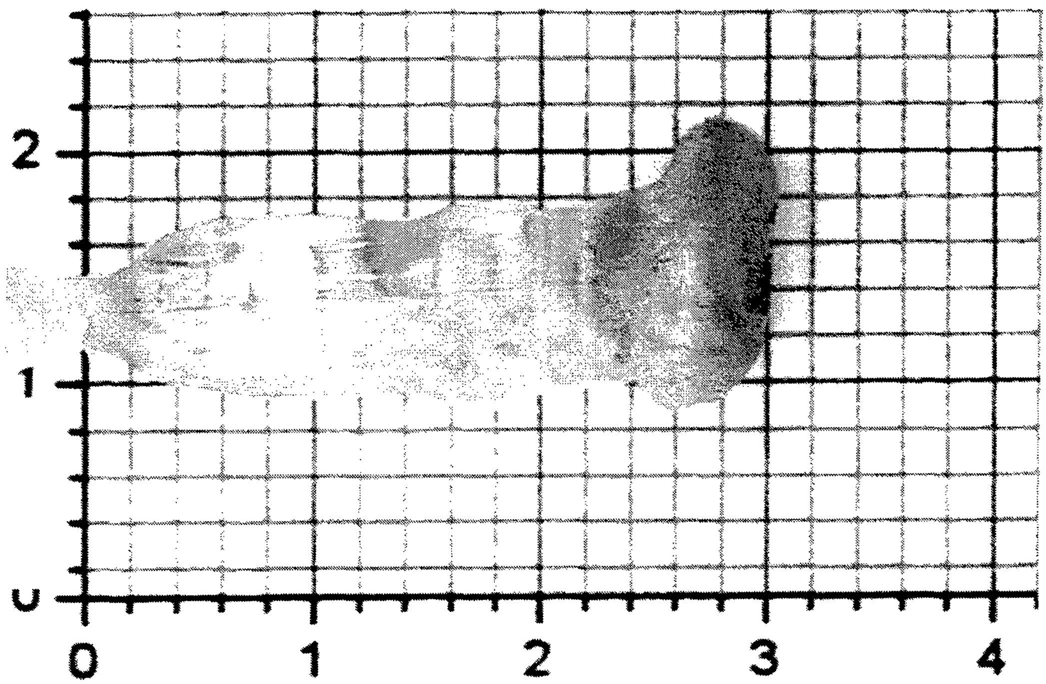
2.1. Critical concentration of the dopant

Complex compound $BaMgAl_{10}O_{17}$ (BAM) melts incongruently with the peritectic reaction and the melt composition at the peritectic point considerably differs from the BAM formula. It proved possible to grow pure and doped transparent BAM single crystals by the floating zone method.



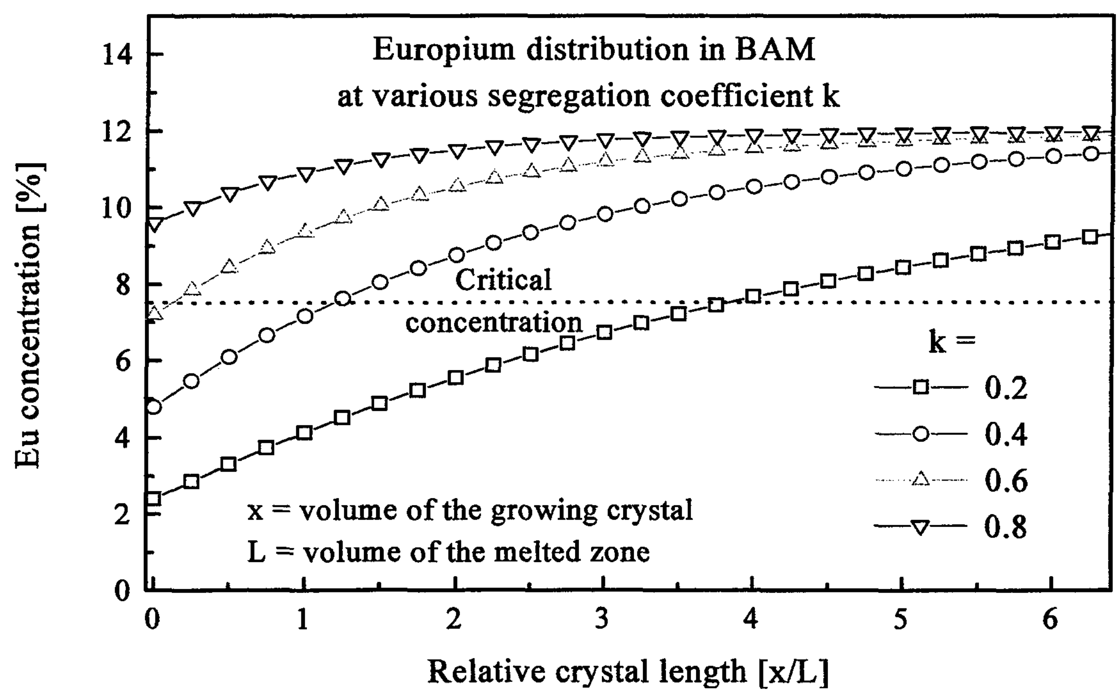


Fig. 1. Image of BAM:Eu crystal (top) and calculated distribution of europium in the crystal for various segregation coefficients k (bottom).

Determination of the segregation coefficient and influence of the dopant critical concentration on the crystal quality will be shown using the example of BAM:Eu crystal. The crystal has been grown from the sintered rod containing 12 at.% of Eu. The transparent part of the crystal extends over 24 mm; the end of the crystal is not transparent (Fig. 1 top). The concentration of Eu in the crystal determined by Electron Probe Microanalysis (EPMA) method at the beginning of the crystal -0 mm in the picture equals 2.4% Eu, it increases to 7.1% Eu near the end of the transparent part –22nd mm and reaches about 43% Eu in the non transparent polycrystalline part at 28th mm.

Dopant concentration in crystals C_s follows the equation:

$$C_s = C_0 - C_0(1-k)\exp(-kx/L) \quad (1)$$

where C_0 is starting concentration in the rod; k segregation coefficient; L volume of the molten drop and x volume of the crystallized part [1]. Distribution of the dopant concentration calculated for various segregation coefficient k is shown in the lower panel of Fig. 1.

Using the plots of Fig. 1 the effective segregation coefficient has been determined to be k_{eff}=0.2. Distribution of Eu in the imaged crystal is shown in the graph by the open squares plot, the horizontal axes of both parts are adjusted. Because of very low segregation coefficient of Eu in BAM not all europium enters the growing crystal thus its concentration in the molten drop increases rapidly. Eu concentration in the growing crystal increases up to the critical concentration. At growth rate close to zero, the critical concentration limit is 8.6 %. In our case of 2 mm/h growth rate the critical concentration decreases to 7.6% that is the 24th mm in the picture. Above the critical concentration, material solidifies in a polycrystalline form shown in the right end of the top picture of Fig. 1.

The results have been verified in other process starting with the rod containing 8% Eu that allowed to grow transparent crystals.

3. ADVANTAGES AND LIMITATIONS OF THE CZOCHRALSKI METHOD

The main advantage of the Czochralski method is the possibility of fast growth of good quality large single crystals. Moreover, since the crystals are grown using oriented seeds they adopt required orientation. In the typical Czochralski arrangements using high frequency generators the metallic crucible heats the melt and the ceramic thermal shields. The need of crucibles seriously limits applicability of the Czochralski method. The platinum crucibles may be used to grow materials melting below 1500 °C and iridium ones below 2100 °C. The ceramic shields are also heated to high temperatures. Pure Al_2O_3 may be used as thermal insulator during crystallizing materials melting below 1750 °C because of the existing radial thermal gradients. Crystallization of higher melting temperature materials requires use of ZrO_2, which withstand crystallization processes of materials melting below 2200 °C. The radial and vertical temperature gradients that exist during crystal growth by the Czochralski method are significantly lower than those in the floating zone method it leads to obtaining crystals with low density of defects.

3.1. Crystal growth rate

Typical crystal growth rates applied in the Czochralski method as well as in other single crystal growth methods from the melt range from several mm/h for simple oxides to less than 1 mm/h for complex oxides as well as heavily doped crystals and solid solutions. The crystal growth rate is limited by diffusion rate of: its component to the crystal/melt interface, intentionally introduced dopants and unintentional admixtures in opposite direction from the melt interface. When the composition of the melt is incorrect, e.g. contains an excess of components which plays a role similar to the dopant then growth rate must be reduced. When the growth rate is to high, a large concentration gradient of the admixtures (dopant, impurities or excessive amount of some components) is created in the melt, and consequently the melt neighboring to the crystal growth region becomes supercooled. As a result, a tendency to spontaneous nucleation appears in the melt in front of the growing crystal, that causes formation of various defects in the crystal.

The crystal growth process by the Czochralski method always begins on a thin seed crystal with convex crystal/melt interface. When the crystal diameter increases the growth rate in the central part of the interface also increases and is higher than the actual pulling rate. This increase in the growth rate is a function of the cone angle and the convexity of the crystal/melt interface. At this stage of the crystal growth process the pulling rate must be reduced in order to maintain the growth rate below the critical value.

3.2. Starting melt composition

The chemical composition of crystals grown by the Czochralski method very often slightly differs from the stoichiometric composition of the crystallized material. Such deviations were found and were well documented, for example in rare earth gallium garnets [2, 3].

Determining the composition of the melt one should take into account the evaporation of a volatile component that dissociates at high temperatures. To such materials belong compounds containing Ga_2O_3 like rare earth gallium garnets and rare earth gallium perovskites.

For example GGG single crystal grown by the Czochralski method contains 61.85 mol.% of Ga2O3 instead of stoichiometric composition 62.5 mol.%. Optimal starting composition is between these two values (about 62.2 mol.%) [2-4]. Therefore, during crystal growth the melt becomes enriched in Ga2O3 when crystal is puled from the melt. Fortunately, this enrichment is compensated by thermal dissociation and subsequent evaporation of Ga2O3.

In case of some materials like gehlenites [5] or crystals with the K_2NiF_4 structure [6], growing good quality crystals from stoichiometric melts is very difficult or almost impossible. If one starts from stoichiometric composition only small part at the beginning of the crystal will be transparent. Since the deviation from the soichiometric composition is not known for most of the crystals, it has to be determined.

The relative change in crystal composition along crystal growth direction determined by EPMA method varies in some direction, consequently the melt composition changes in the same direction. It means that the initial composition has to be changed in the opposite direction. This procedure has to be repeated until the crystal is transparent throughout its whole length and the concentration of elements measured on the slice along the crystal growth direction does not reveal significant changes.

3.3. Segregation coefficient

Segregation of the dopants is yet another disadvantage of the Czochralski method. It leads to a difference in composition between the crystal and the melt if the segregation coefficient differs from one. In order to pull single crystals with a specific desired dopant concentration, it is needed to know the segregation coefficient of the dopant in the particular melt.

We have determined the segregation between neodymium and lanthanum along growth direction of $La_{1-x}Nd_xGaO_3$ single crystals [7]. Concentration of components measured on slices cut from single crystals along the growth direction, versus parameter g describing the part of crystallized material is shown in Fig. 2. Concentration of admixture in mol.% along growth directions, versus parameter g describing the part of crystallized material follows [8] the equation:

$$C_s(g) = k_{ef}C_o(1-g)^{kef-1} \qquad (2)$$

where: k_{ef} is the effective distribution coefficient; C_o starting admixture concentration in the melt and g ratio of the crystal mass to the total starting mass in the crucible. The effective segregation coefficient of Nd in $La_{1-x}Nd_xGaO_3$ solid solutions is about 0.77 and is reciprocal to La segregation in $NdGaO_3$ (k_{eff}=1.30).

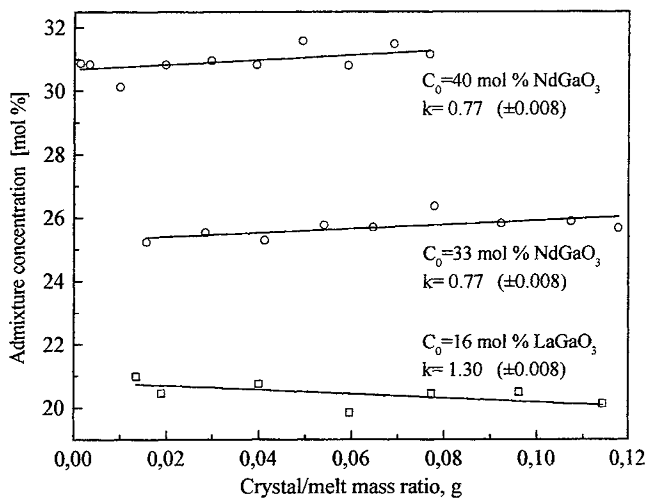


Figure 2. Determination of segregation coefficient in solid solutions crystals grown by the Czochralski method.

3.4. Phase transition temperature dependence

The orthorhombic to rhomboedral first order phase transition that occurs at 150 C in pure LaGaO3 [9] have been studied as a function of Nd and Pr concentration [7, 10]. It has been found that the temperature of the first order phase transition increases linearly with the dopant concentration with the rate of 20.5 °C/mol.% Nd and 13.3 °C/mol.% Pr, respectively.

The temperature of the phase transition in $La_{1-x}Nd_xGaO_3$ and $La_{1-x}Pr_xGaO_3$ as function of the unit cell volume increases linearly while orthorhombic unit cell volume almost linearly decreases with Nd/Pr concentration x. It implies that transition temperature T_{tr} linearly rises with the unit cell volume V_{ort}. It is interesting that both plots are almost identical. We are unable to tell whether it is merely accidental coincidence or has any deeper meaning since the X-ray diffraction has been measured only at room temperatures. Analysis of deformation of the perovskite unit cell and gallium oxygen GaO_6 octahedron as a function of dopant concentration indicates that both La and Pr ions are too small to form the cubic lattice.

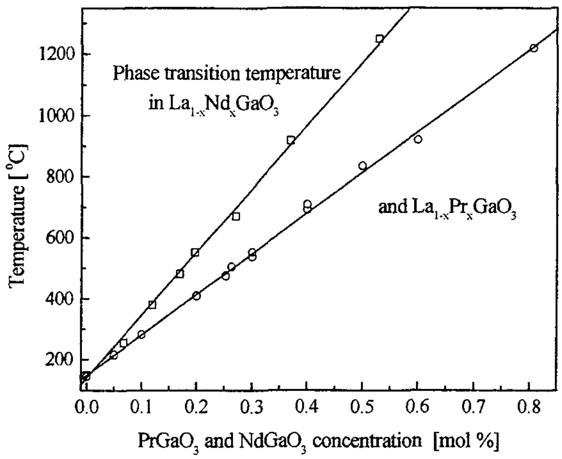


Figure 3. Phase transition temperature dependence in $La_{1-x}Nd_xGaO_3$ and $La_{1-x}Pr_xGaO_3$.

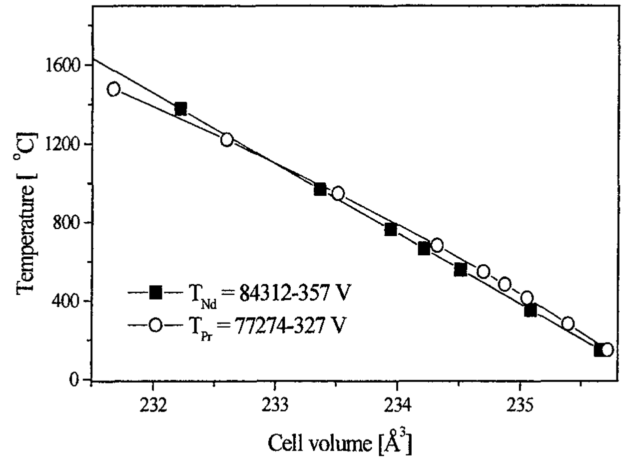


Figure 4. The phase transition temperature in $La_{1-x}Nd_xGaO_3$ and $La_{1-x}Pr_xGaO_3$ as function of the unit cell volume.

3.5. Rare earth ions and strontium in $LaGaO_3$

We have also investigated other isomorphous rare earth elements apart from Pr and Nd such as Sm, Eu and Er in $LaGaO_3$ single crystal and non-isomorphous doping by Sr. It has been found that only Pr and Nd galates form solid solutions in the whole concentration range with $LaGaO_3$. The solubility limit decreases to around 20 at. % for Sm, about 1.6 at. % for Eu and only to around 0.4 at. % for Er. The solubility limit for non-isomorphic substitution of La by Sr is approximately 12 mol.% while up to about 1.5 mol.% the introduced admixture behaves as isomorphic substitution. From the determined segregation coefficient for Sr, Pr, Nd Eu and Er in $LaGaO_3$ it has been found that the value of the segregation coefficient varies linearly with the substituting ions radii.

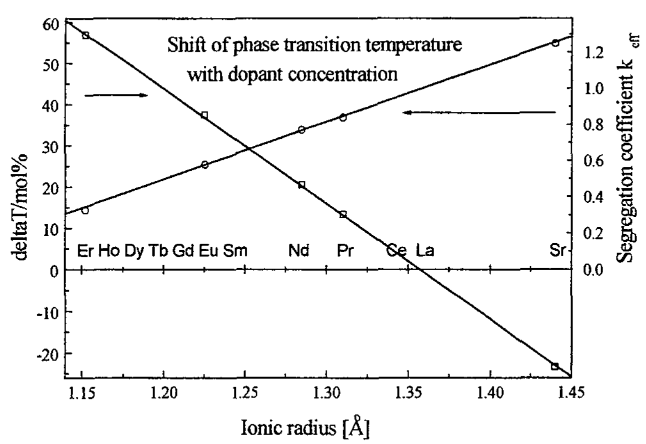


Figure 5. Segregation coefficient of Sr, Pr, Nd, Eu and Er in $LaGaO_3$ and shift of phase transition temperature with dopant concentration versus substituting ions radius.

Substitution of La by Eu or Er also increases the first order phase transition temperature faster than Pr or Nd; substitution of La by Sr decreases the temperature of the phase transition. Preliminary measurements suggest that the rate of the phase transition temperature shift with dopant concentration may be also a linearly vary with the ionic radius of the substituting element.

3.6. Cubic perovskite solid solutions

Results previously published [11-15] and our investigations [7, 10] prove that cubic perovskites that do not undergo any phase transitions should be searched for in the crystals based on strontium perovskites such as $SrAl_{0.5}Ta_{0.5}O_3$ (SAT) and $SrAl_{0.5}Ta_{0.5}O_3$ (SAN). The typical representative of this group of solid solutions is (1-x)*SAT:x*LA (LA=$LaAlO_3$). We have performed preliminary crystal growth processes using floating zone and the Czochralski methods for x = 0, 10, 20, 22, 25, 30, 50, 60 and 66.6 mol.% of lanthanum aluminate concentration. The crystals adopt cubic structure at x up to 0.50 with the half of lattice constant varying from 3.895 to 3.845 Å (Fig. 6), while at x=66.6 the structure changes to rhombohedric.

To grow crystals by the Czochralski method we used <111> and <100> oriented seeds, pulling rate of 2 mm/h, rotation rate 20 rpm and used 40 mm diameter iridium crucible. The 18 mm in diameter crystals grown from the melt containing 22 mol.% and

more lanthanum aluminate were light yellow if the processes were carried out in pure nitrogen with oxygen level in the output gas below 500 ppm. The crystals adopt dark yellow color in case of insufficient thermal insulation or in case of unidentified reasons leading to higher oxygen concentration in the output gas. The crystals grown with starting composition of 20 mol.% and less of LA were dark, almost not transparent and they had tendency to unstable growth (e.g. spiral growth) increasing with lowering of LA concentration. Images of two crystals are presented in Fig. 7.

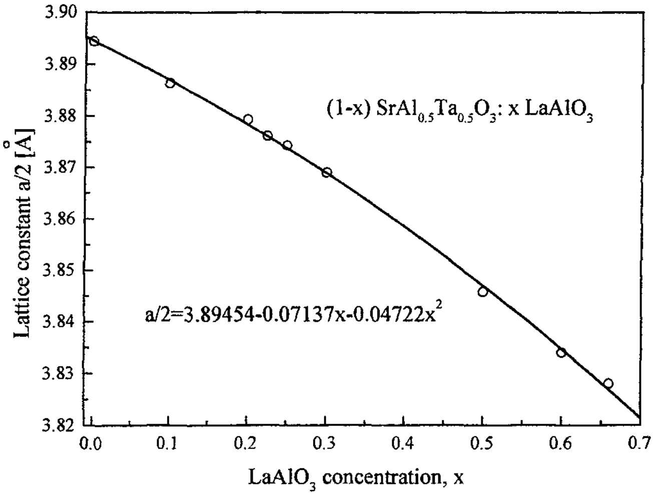


Figure 6. Dependence of the lattice constant on $LaAlO_3$ concentration in $SrAl_{0.5}Ta_{0.5}O_3$:$LaAlO_3$ solid solutions.

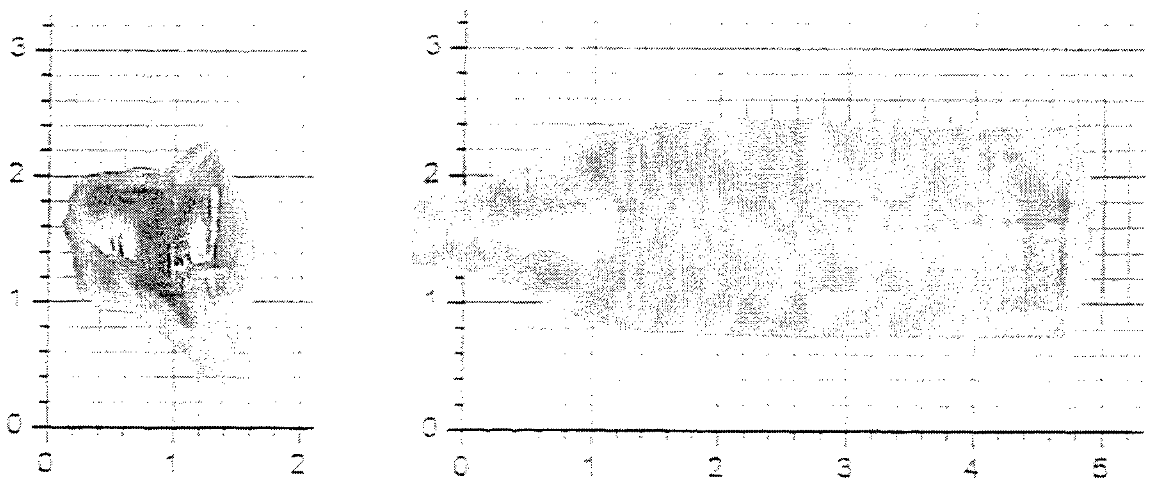


Fig. 7. Solid solution crystals (1-x)*$SrAl_{0.5}Ta_{0.5}O_3$:x*$LaAlO_3$ grown by the Czochralski method, x=0.2 (left) and x=0.25 (right).

4. CONCLUSIONS

The Czochralski and floating zone methods have been compared and types of compounds that can be crystallized by either of them have been discussed. To the main problems influencing crystal quality discussed here belong temperature gradients, maximum crystal growth temperature, growth atmosphere, melt dissociation and dopant segregation.

The floating zone method allows one to crystallize also many compounds exhibiting peritectic point reaction. The crystallization may be carried out in any atmosphere even in air or oxygen thus decreases dissociation of the melt. Thus in comparison with the Czochralski method, it may be applied to much wider range of materials. The segregation of the dopant is less important here. Since this method does not require any crucible, it may be used to grow crystals with higher melting temperatures. In addition, the problems of reaction between the melt and crucible are avoided.

The main disadvantage of the floating zone method results from the large temperature gradient along the crystal. In consequence, the quality of the crystals is lower than of those grown by the Czochralski method.

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